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Relativistic model potential for a number of heavy elements

M NANDI AND S. CHATTERJEE

Indian Association for the Cultivation of Science, Jadavpur, Calcutta-32

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The non relativistic theory of model potential has been very successful in explaining physical properties of many solids. In this work we generalise the model potential theory to the relativistic case also. With this new formulation we have calculated the model potential parameters for 18 heavy elements. The results show that there are splittings in the model potential parameters for p and d states—the splittings being maximum for Hg and minimum for Rb.

1 INTRODUCTION

For the last ten years the study of the model potential parameters has been extensively performed by a group of workers (Heine & Abarenkov 1964, Animalu & Heine 1965, Abarenkov & Heine 1965). The essential idea is, however to assume the ionized atom, stripped of its valence electrons, to have a region inside an inscribed sphere of radius R_M where the potential is constant and l-dependent; outside the inscribed sphere, however, the potential is assumed to be $-2z/r$ or in other words

$$\left.\begin{aligned} V(r) &= -\sum_l A_l(\epsilon) P_l && \text{for } r \leqslant R_M \\ &= -2z/r && \text{for } r > R_M \end{aligned}\right\} \quad \ldots (1)$$

where P_l is the projection operator that picks out the component of the wave function with angular momentum l, and z is the valence of the ion. The coefficients $A_l(\epsilon)$ are found out with the help of quantum defect method. This is achieved by comparing the logarithmic derivatives found out at R_M for the constant potential solution of the radial Schroedinger equation.

The equation then becomes with $X = R_M(A_l - |\epsilon|)^{\frac{1}{2}}$

$$\frac{X j_{l-1}(X)}{j_l(X)} - l = D^l/U^l \quad \ldots (2)$$

where U^l and the derivative D^l are the solutions of the radial part of the Schroedinger equation. Recently, however, it has been shown (Chatterjee & Chatterjee 1974) that a relativistic generalization of this model potential theory can be made. According to this theory each of the model potential parameters (except $l = 0$) will be split according to the value of $K = \pm l$ because of the spin-orbit splitting of those term values. These splittings will naturally be more for the

heavier elements where the relativistic effects are more prominent. In this work we have calculated the relativistic model potential for a number of heavy elements and compared them with the nonrelativistic values of Animalu & Heine (1965).

2. Formulation

The model potential in the nonrelativistic case is given by eq. (1) and is found out from the solution of eq. (2), where the derivative D^l and the wave function U^l are found out from the relation

$$\left.\begin{aligned} U^l &= {}^0U^l - \tan \pi\eta_l {}^1U^l \\ D^l &= {}^0D^l - \tan \pi\eta_l {}^1D^l \end{aligned}\right\} \quad \ldots (3)$$

where ${}^0U^l$ and ${}^1U^l$ are the regular and the irregular solution of the radial part of the Schroedinger equation given by

$$\frac{d^2U^l}{dr^2} + \left[\epsilon + \frac{2}{r} - \frac{l(l+1)}{r^2}\right] U^l = 0 \quad \ldots (4)$$

and η_l is the η defect found out from the spectroscopic term values of the ion (Ham 1955). For relativistic case however eq. (4) is replaced by two first order differential equation (Loucks 1965)

$$\frac{d(cf)}{dr} = \frac{K-1}{r} cf - (\epsilon - V)g \quad \ldots (5a)$$

$$\frac{dg}{dr} = \left(\frac{\epsilon - V}{c^2} + 1\right) cf - \frac{K+1}{r} g \quad (5b)$$

By writing $U_1 = rcf$ and $U_2 = rg$ and eliminating U_1 from eqs. (5a) and (5b) (Chatterjee & Chatterjee 1974) we get

$$\frac{d^2U_2}{dr^2} + \left[(\epsilon - V) - \frac{K(K+1)}{r}\right] U_2 = 0. \quad \ldots (6)$$

This equation resembles eq. (4) for $V = -2/r$ with l replaced by K which takes all integral values positive and negative except zero. So all the relevant theories of the non-relativistic Q D M. can be applied to the relativistic case. In that case one needs to calculate the quantity cf_k/g_k given by

$$\frac{cf_k}{g_k} = (K + D^k/U^k) R_M \quad \ldots (7)$$

where for $J = l+\frac{1}{2}$, $K = -l-1$ and for $J = l-\frac{1}{2}$, $K = l$. R_M is the radius of the inscribed sphere outside which the potential is hydrogen like. U^k is the solution of eq. (6) D^k and U^k are given by

$$\left.\begin{aligned} U^k &= {}^0U^k - \tan \pi\eta_k\, {}^1U^k \\ D^k &= {}^0D^k - \tan \pi\eta_k\, {}^1D^k \end{aligned}\right\} \qquad \ldots \quad (8)$$

η_k are to be found out from the atomic spectra which contains the fine structure splitting (Chatterjee & Chatterjee 1974) Similar to the nonrelativistic case if we define the relativistic model potential as

$$\left.\begin{aligned} V(r) &= \sum_k A_k(\epsilon) P_k \qquad \text{for } r \leqslant R_M \\ &= -2z/r \qquad\qquad \text{for } r \geqslant R_M \end{aligned}\right\} \qquad \ldots \quad (9)$$

we have the model function inside R_M as plane waves given by

$$\psi^m(\boldsymbol{k}, r) = \left(\frac{1+k^0}{2k^0}\right)^{\frac{1}{2}} \begin{pmatrix} \chi(m) \\ \dfrac{\sigma.\boldsymbol{k}}{1+k^0}\,\chi(m) \end{pmatrix} e^{i\boldsymbol{k}\cdot\boldsymbol{r}} \quad (m = \pm\tfrac{1}{2}) \qquad \ldots \quad (10)$$

outside R_M the solution is given by

$$\psi_{k\mu}(\rho) = \sum_{k,\mu} A_{k\mu} \begin{pmatrix} g_k(\rho)\, \chi_k{}^\mu \\ i f_k\,(\rho)\, \chi_{-k}{}^\mu \end{pmatrix} \qquad . \quad (11)$$

If we want to match these two solutions at the boundary of the sphere of radius R_M we will have to take the expansion of eq (10) in spherical waves

$$\psi^m(\boldsymbol{k}, r) = \sum_{k,\mu} a^m{}_{k\mu} \begin{pmatrix} j_l(\boldsymbol{k}\rho)\chi_{kk}{}^\mu \\ i\boldsymbol{k} S_k \\ 1+k^0 \end{pmatrix} \qquad . \quad (12)$$

In order to make eqs. (12) and (11) join smoothly we make the condition (in a u)

$$\frac{\boldsymbol{k} S_k j_l'(\boldsymbol{k} R_M)}{j_l(\boldsymbol{k} R_M)} = \frac{C f_k}{g_k} \qquad \ldots \quad (13)$$

where S_k is positive or negative as K is positive or negative and $l = K$, $l' = K-1$ for $K > 0$ and $l = -K-1$, $l' = -K$ for $K < 0$.

Now for a particular model potential parameter A_k, writing

$$X = kR_M = R_M(A_k - |c|)^{\frac{1}{2}}$$

we have

$$XS_{kjl}'(X)/j_l(X) = K + D^k/U^k \qquad \ldots (14)$$

Thus by finding out the quantity D^k/U^k from the relativistic quantum defect method one can easily find out the A_k as a function of energy

3 Result and Discussion

Table 1 gives the relativistic model potential parameters for some heavy elements calculated by eq. (14) along with the nonrelativistic values of Animalu & Heine (1965) at the Fermi energy The spectroscopic term values were taken from Moore (1949, 1952, 1958) The subscripts $K = -1$ corresponds to the $l = 0$ of the nonrelativistic case Similarly $K = -2$ and $+1$ and $K = -3$ and $+2$ refers to the $l = 1$ and 2 corresponding to p and d states The Fermi energy has been taken from the graphs given by Animalu (1973) This table does not contain the transition metals because they do not obey the ordinary quantum defect law However recently Animalu (1973) has obtained a new quantum defect law which explains the transition metal spectrum Although the preliminary observation indicates the possibility of application of this law

Table 1 Parameters for model potential (a u)

Metal	R_M	Relativistic					Non-Relativistic			Z
		A_{-1}	A_{-2}	A_1	A_{-3}	A_2	A_0	A_1	A_2	
Rb	4·6	0 224	0 225	0 227	0 383	0 386	0 224	0 226	0·384	1
CS	4 9	0·205	0 199	0 212	0 345	0·370	0 205	0 207	0 366	1
Ca	2 6	0·540	0 495	0·515	1·488	1·492	0 540	0 500	1·490	2
Ba	3 4	0·450	0·335	0·375	1 050	1·090	0 450	0·340	1·070	2
Zn	2·2	0·990	1·130	1·160	0 970	0·995	0 990	1·140	0·980	2
Cd	2 6	0·880	0 960	1 020	0·850	0·900	0 880	0·980	0·870	2
Hg	2·6	0 970	0·960	1·360	0·800	0 960	0·970	1·110	0 850	2
Ga	2·4	1·440	1·560	1·600	1 408	1 411	1·440	1 580	1·410	3
In	2·4	1·320	1·420	1·500	1·080	1 100	1·320	1·460	1·100	3
Tl	2 4	1 440	1·350	1·650	0·960	1 000	1 440	1·510	0·980	3
Ge	2·0	2·100	2·310	2·360	2 080	2 100	2·100	2·340	2·090	4
Sn	2·0	1·840	2 010	2·100	1·610	1 630	1 840	2 040	1·620	4
Pb	2·1	1·920	1·900	2·100	0 895	0·905	1·920	2·000	0·900	4
As	2 0	2·710	2·990	3·120	1 990	2·010	2 710	3·080	2·000	5
Sb	2·0	2 420	2·640	2 680	1 798	1·802	2·420	2·660	1·800	5
Bi	2·0	2·380	2 500	2 698	0·248	0·252	2·380	2·580	0·250	5
Se	2·0	3·420	3·740	3 790	2·990	3 030	3·420	3·770	3·000	6
Te	2·0	3·040	3 300	3·360	2·799	2·801	3·040	3·320	2·800	6

to the relativistic case also, we have presently not included them in this work. If we go through the table 1 we notice that in general p levels have more splitting than the d levels Amongst these again Hg, Tl, Bi and Pb have considerable splitting while Rb has the lowest splitting. Amongst these largest spiltting elements the model potential parameters of Bi and Pb are a little bit uncertain because of nonavailability of sufficient number of term values In these cases extrapolation was done in the same way as was done by Animalu & Heine (1965). But in the case of Hg and Tl there are sufficient number of term values, and hence the model potential parameters could be extrapolated more reliably to the Fermi energy. This may be the reason why there are more splitting of A_1 and A_{-2} in Hg and Tl than Bi and Pb, although the splitting in the term values of Bi and Pb are more From these parameters one can easily construct the pseudopotential form factors for these materials and hence relativistic band structure and probably the phonon spectrum can be obtained We hope to achieve this goal in near future.

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